EUROPEAN PATENT APPLICATION

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(54) Membrane system.

(57) A new type of polymeric microporous membrane has been synthesized which is distinguished by a highly-branched porespace morphology that is continuous and triply-periodic, and thus very precisely controlled and easily characterized. The membrane consists of a polymeric matrix containing pores of diameter on the order of 10 nm connected into a continuous pore network exhibiting long-range three-dimensional order. This long-range order is evidenced in small-angle X-ray scattering (SAXS) experiments by Bragg reflections that index to a triply-periodic space group, as well as in electron micrographs that match predictions from a theoretical model of the same space group and lattice parameter. The membrane combines three important features that have not been present simultaneously in any prior art membrane having pore diameters between 2 nm and 1 micron. First, the pores are identical in size and shape to a very high degree, and their size can be controlled in the synthesis. Second, the porespace is characterized by intricate branching and reconnections, with at least three pore throats meeting at a given pore body, this number (the coordination number) being the same for each pore body, and the porespace is isotropic in the cases where the space group is cubic. These two features allow accurately controlled sieving on the basis of particle size and shape, and provide highly accessible and precisely shaped pore bodies and surfaces for other applications such as catalysis, ion exchange, and the preparation of metal microstructures. And third, the membrane has a high porosity -- approximately 90% -- so that high rates of throughput can be reached. In addition, the membrane can be produced from certain microstructured fluid phases that are thermodynamic equilibrium states, so that it can be produced inexpensively and reliably.

EP 0 292 325 A2

Description

MEMBRANE SYSTEM

Field of the Invention:

5   The present invention is in the field of microporous membrane materials, especially polymeric membranes.
The past 20 years has seen tremendous growth in the applications of polymeric membranes, not only in filtration -- microfiltration (MF), ultrafiltration (UF), and hyperfiltration or reverse osmosis (RO) -- but also in a variety of other areas such as fuel cells and batteries, controlled-release devices as for drug or herbicide metering, dialysis and electrodialysis, pervaporation, electrophoresis, membrane reactors, ion-selective
10   electrodes, and as supports for liquid membranes, to name some important areas. Furthermore, modification of neutral polymer membranes can yield ionomeric or 'ion-exchange' membranes which are finding increasing application in many chemical, electrochemical, filtration and even biochemical processes. In many applications the availability of a membrane with precisely-controlled porespace and high porosity would represent a significant technological advance.

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Background Art:
. The ultimate membrane would have identical, highly interconnected pores comprising a porespace with perfect three-dimensional periodic order. This ideal has been approached in the development of polymeric microporous membranes but never achieved. The simplest type of sieve is a net filter, where each layer in the
20   filter is a woven mesh. The geometry of the pore space in a given layer is thus a close approximation to a finite portion of a doubly-periodic net, the latter being a mathematical idealization with perfect regularity within the plane. Note that if, in addition, these doubly-periodic layers are stacked at regular intervals with all layers in vertical registry, the resulting sieve is triply-periodic. Woven mesh filters are not available with pore sizes less than about 60 microns, so they cannot be used for reverse osmosis, ultrafiltration, nor even microfiltration.
25   Another doubly-periodic geometry that is achieved in some filters is that of hexagonally close-packed cylindrical pores. For example, glass capillary bundle filters are made from close-packed arrays of parallel glass capillaries. Capillary arrays can also be formed from hollow fibres of organic polymers, although these are not yet available commercially. A major drawback of cylindrical-pore filters is the lack of porespace branchings and reconnections, which leaves only one pathway for a fluid particle entering a given pore; thus
30   clogging becomes a serious problem, as does sensitivity to handling. Of course, cylindrical pores can provide a narrow distribution of pore sizes without necessarily lying on a doubly-periodic lattice; for example, nucleation-track filters have randomly placed parallel cylindrical pores. But this randomness means that the number of pores per unit cross-sectional area must be kept small to maintain monodispersity, so that these filters have the additional drawback of low porosity and thus low filtration rates. Nevertheless, nucleation-track
35   filters are considered the best membrane filters available for sieving below 60 microns, despite these obvious drawbacks.
U. S. Patent no. 4,280,909 describes a microporous membrane which is, strictly speaking, triply-periodic, but the topology of the porespace is exactly the same as in the capillary array membranes, namely the flow channels are strictly linear and there are no porespace branchings or reconnections. The periodicity in the
40   third dimension refers only to the vertical stacking of tapered pores of equal height, so that the cylindrical pores of the capillary array membrane have become instead tubular pores with a periodically varying diameter. This membrane does not satisfy one of the most important desired features, namely the intricate yet controlled porespace. A precisely defined porespace with branching and reconnections, in which each identical pore body connects to exactly the same number of other pore bodies through identical pore throats, is important in:
45   a) reducing clogging, as when the membrane is used for filtration, for example;
b) enhancing mixing, as when the membrane is used in catalysis or ion exchange, for example; and,
c) providing accessible channels and pore bodies of specific shape, as when the membrane is used in the preparation of metal microstructures [Jacobs et al. 1982], for example.
Sintered-particle membranes have intricate three-dimensional porespaces with many interconnections, but
50   have oddly-shaped and polydisperse pores as well as low pore density, the latter drawback being the primary reason they have been generally replaced by membrane filters. Most sintered-particle filters have retention ratings at or above 0.7 microns.
The membrane that is most commonly used in particle filtration has high porosity but a random, irregular porespace that makes it generally unusable as a sieve. Distributions of pore radii in cellulose nitrate membrane
55   · filters have been measured using mercury porisimetry, and the distributions, are very broad: the full-width at half-maximum (FWHM) of the distribution is about equal to the average radius [Brock 1983].
In the realm of nonpolymeric sieves, zeolites provide fairly well-controlled, triply-periodic pore networks, but the free diameters of aperatures governing access to channels are generally less than 2nm, and in fact nearly always less than 1nm [Barrer 1978]; also the porosities of zeolites (defined as cc's of water per cc of crystal)
60   are nearly always less than 50%. Furthermore, most zeolites selectively absorb polar molecules because most are themselves highly polar, having high local electrostatic fields and field gradients [Barrer 1978]. Perhaps most importantly, the macroscopic size of zeolite crystals has very serious practical limitations making such materials unsuitable for forming reasonably large membrane-like structures with the necessary degree of

continuity.

These and other difficulties with prior materials and methods have been obviated in a novel and inventive manner by the present invention.

The invention resides in a polymeric, microporous material characterized by: a continuous, highly branched and interconnected porespace morphology and having a globally uniform pore size and substantially identical   5
pore bodies and pore throats.

The invention involves a polymeric, microporous material characterized by a continuous, highly regular, preferably triply-periodic, highly branched and interconnected pore space morphology having a globally uniform, pre-selected pore size. The pore size ranges from one, or preferably two nanometers to sixty microns, preferably in the range of one, or preferably two nanometers to one micron and particularly preferably   10
on the order of ten nanometers. The material of the invention is characterized by high porosity: greater than fifty percent and, for certain applications, greater than ninety percent. The invention involves controlled variation of the pore characteristics, particularly the electro-chemical characteristics.

The material preferably has at least 3 pore throats per pore.

The material preferably has substantially identical pore bodies, and substantially identical pore throats.   15

The pore bodies are preferably of a predetermined shape.

The pores may have pre-chosen local electrostatic fields and field gradients, and are adapted to retain a pre-chosen degree of affinity for polar molecules. Preferably, the membrane material has substantially zero affinity for polar molecules. The polymer may be formed from an ionomer, the membrane material being characterized by electrically charged pores.   20

The polymer may be electrically conducting.

The membrane material may comprise two bicontinuous pore systems separated by a matrix having two sides, each side having a different ion selectivity.

The pores may be at least partly filled with a fluid agent for active or passive controlled release, for example for controlled drug release.   25

The membrane material may form a filter, having a first fluid on one side, and a fluid with substantially different characteristics on the other side.

The invention involves several related methods for forming microporous materials, including polymerization of the hydrophobic component in a ternary sufactant/water/hydrophobe cubic phase, and other thermodynamically stable or metastable phases of phase-segregated systems, especially systems which are   30
substantially ternary or binary.

One such method is set out in Claim 5.

The polymerization may be carried out by a radical chain polymerization, or using catalytic polymerization, or by photochemical induction.

Further methods are set out in Claims 6 to 12.   35

In the methods of Claim 11 or 12, the porosity of the first microporous material is preferably less than 50 percent so that the porosity of the second material is more than 50 percent. Preferably, the first microporous material has a porosity less than 10 percent so that the second material will have a porosity greater than 90 percent.

Materials of the invention can be used for example as membranes to segregate virus-sized particles from   40
other components of a fluid, the pore size of the material being smaller than the virus size to retain the viruses, or larger than the virus size, so as to pass the virus particles. A particular use of the material is to segregate the human immunodefficiency virus (HIV) from blood components. Another important use of the material involves enzymes and other proteins immobilised in the structure of the material.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows small-angle x-ray scattering data from membrane material according to the present invention. Individual marks represent recorded intensities at each channel. Vertical lines indicate   50
theoretical peak positions for a structure of space group Im3m and lattice parameter 11.8 nm. The label on the abscissa is $s = 2 \sin (\text{theta})/\text{lambda}$, where theta is one-half the scattering angle and lamda is the wave length of the radiation used. The large peak at $s = .0025/\text{Angstrom}$ is due to the main beam, and is not a reflection.

FIG. 2 shows an electron micrograph of membrane material according to the invention. Dark regions   55
correspond to PMMA, and light regions to void. Regions of particularly good order are outlined. (Magn. 1,000,000).

FIG. 3 is the optical diffraction pattern of the negative use to make FIG. 2. The eight-spot pattern indicated with circles provides further demonstration of cubic symmetry.

FIG. 4 A,B, and C are computer-generated pictures of a theoretical model structure, from Anderson,   60
1986, the applicant's doctoral thesis. The surface has constant mean curvature, and divides space into two interpenetrating labyrinths, one threaded by graph A and the other by graph B.

. A) (upper). Computer graphic, viewed approximately along the (110) direction.

B) Projection in the (111) direction.

C) (lower). Line drawing, without hidden line removal, from an oblique angle.   65

FIG. 5 A and B show digitized electron micrograph of:

A) a bicontinuous cubic phase in a star-block PI/PS copolymer, and

B) a prediction using a bicontinuous model from the applicant's doctoral thesis, Anderson, 1986.

The model used was determined by the constant-mean-curvature surface of the "D" family (Pn3m symmetry) which matches the volume fractions of the sample. A computer was used to send projection rays through the theoretical model, and the grey level at each pixel calculated.

FIG. 6 combines the views of FIGS. 5 A and B for clearer comparison.

FIG. 7 sets out thre equations used in the calculation of the behaviour of block copolymers.

DETAILED DESCRIPTION OF INVENTION

A bicontinuous morphology is distinguished by two interpenetrating, labyrinthine networks of ordinarily immiscible substances [Scriven 1976], in which macroscopic phase separation is prevented by one of at least two possible means: 1) chemical linking between the two components, as in block copolymers; or 2) addition of surfactant. A triply-periodic bicontinuous morphology (TPBM hereafter) is further distinguished by long-range three-dimensional periodic ordering conforming to a space group. TPBMs were proposed in the late 1960's and 1970's as possible microstructures in binary surfactant/water 'cubic phases' [Luzzati et al. 1968; Lindblom et al. 1979], and in ternary surfactant/water/oil cubic phases [Scriven 1976] (cubic phases are also known as 'viscous isotropic phase' liquid crystals). This has been fairly well established for certain binary cubic phases [Longely and McIntosh 1983; Rilfors et al. 1986], but until this disclosure, demonstrated with less certainty in the case of ternary cubic phases [Anderson 1986; Fontell et al. 1986; Rilfors et al. 1986]. TPBM's have also been demonstrated in phases of cubic symmetry occuring in block copolymers [Alward et al. 1986; Hasegawa et al. 1986]. Described herein is the first polymeric microporous membrane with a highly-branched, triply-periodic network of submicron pores, which has been produced by radical chain polymerization of the oleic component (e.g. methyl methacrylate) of a ternary surfactant/water/polymerizable oil cubic phase.

"Binary" and "Ternary":

In this description, it should be noted that when the terms "binary system" or "ternary system" are used, they are not meant to exclude systems in which additional components are present but do not affect the development of the desired phase-segregation. For example, components may be present in such small relative quantities that the system is equivalent to a binary or ternary system for the purposes of this invention. Furthermore, one component may consist of sub-components which present nearly identical phase characteristics or which together present a single phase characterisic without departing from this invention. Thus, for example the definition includes a ternary hydrophobe/water/surfactant system whose water portion is a 50-50 mix of water and deuterated water and/or whose hydrophobic component is a mix of sub-components which segregate substantially together under the fabrication conditions to be applied.

The procedure used to produce the first example began with a mixture of 1 gm of the surfactant didodecyldimethylammonium bromide (DDDAB; the registry number of DDDAB is 3282-73-3), 1.4 ml of distilled water, and 0.26 ml of methyl methacrylate (MMA) which had been purified by vacuum distillation and to which had been added 0.004 gm/ml of azobisisobutyro-nitrile (AIBN). The mixture was stirred vigorously with a magnetic stir bar in a capped vial (when styrene was used instead of MMA, stirring had to be very gentle). After a few minutes magnetic stirring became impossible because of high viscosity, which together with optical isotropy as checked by observation between crossed polarizing lenses indicate a cubic or 'viscous isotropic' phase. At approximately the same volume fractions but with alkanes such as decane or dodecane, cubic phases have been reported by Fontell et al. [1986] and by the present author [Anderson 1986], verified in both cases by Small Angle X-ray Scattering. After equilibrating for a week at 23C, the mixture was smeared onto the end of the plunger of a large syringe, and pushed through an 18 gauge needle into a 1.5 mm l. d. X-ray capillary. After loading and sealing of the capillary, the sample remained clear and optically isotropic. The optical isotropy of cubic phases is due to the equivalence of the three principle directions; other liquid crystalline phases are birefringent.

The capillary was then placed in a photochemical reactor having four UV lights, emitting radiation at 350 nm. The sample was exposed for 36 hours, to bring about radical chain polymerization of the MMA via the decomposition of AIBN into initiating radicals. By the end of this time the sample was opaque white in appearance.

The sample was first examined by Small Angle X-ray Scattering. A Kratky small-angle camera equipped with a position-sensitive detector was used, with tube power set at 1000 watts, and data collected for five hours. The result is shown in FIG. 1, and it is clear that distinct Bragg peaks are recorded. This verifies that the sample has long-ranged periodic ordering. In FIG. 1 are indicated the theoretical peak positions for a body-centered cubic space group, Im3m, and it is seen that the theoretical peaks are represented by the data.

Recent self-diffusion measurements on DDDAB/water/dodecane cubic phases at approximately the same composition [Fontell et al. 1986] indicate that the cubic phase is bicontinuous. This was also the conclusion of the present author, with decane as oil [Anderson 1986]. That this is also true of the present phase after polymerization will be shown herein. It should be mentioned that the present applicant has shown [Anderson

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Claims

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1. A polymeric, microporous material characterized by:

a continuous, highly branched and interconnected porespace morphology and having a globally uniform pore size and substantially identical pore bodies and pore throats.

2. A polymeric, microporous material characterized by: 15

a continuous, highly branched and interconnected porespace morphology and having a globally uniform pore size and substantially identical pore bodies and pore throats, the pores being at least partially filled with a fluid agent for active or passive controlled release.

3. A polymeric, microporous material characterized by:

a continuous, highly branched and interconnected porespace morphology and having a globally 20 uniform pore size and substantially identical pore bodies and pore throats, the material formed into a filter with a first and second side with a first fluid on the first side and a fluid with substantially different characteristics on the second side.

4. The material of claim 1, 2 or 3 in which the said porespace morphology is triply periodic.

5. A method of manufacturing a highly regular, preferably triply-periodic, microporous material 25 characterized by:

polymerization of a polymerizable hydrophobe in a ternary surfactant/water/polymerizable hydrophobe cubic phase or of the polymerizable surfactant of a binary water/surfactant cubic phase.

6. A method of manufacturing a highly regular, preferably triply-periodic, microporous material characterized by: 30

a. the formation of a triply-periodic, bicontinuous fluid phase in thermodynamic equilibrium state of a ternary surfactant/water/hydrophobic polymer system in which the polymer is above its melting point followed by

b. a cooling of the polymer to below its melting point.

7. A method of manufacturing a doubly-periodic, microporous material characterized by the 35 polymerization of the oleic component of a binary or ternary hexagonal phase.

8. A method of manufacturing a doubly-periodic, microporous material characterized by the chemical erosion of one component of a block copolymer cylindrical phase.

9. A method of manufacturing a doubly-periodic, microporous material characterized by the chemical erosion of one component of the cubic phase of a block copolymer. 40

10. A method of manufacturing a doubly-periodic, microporous material characterized by the chemical erosion of one substituent of a single component cubic phase.

11. A method of manufacturing a highly regular, preferably triply-periodic, second microporous material characterized by the steps of:

a. infiltrating a polyerizable monomer into the pores of a first highly regular, preferably 45 triply-periodic, microporous material having a chemically erodible original substrate material.

b. polymerizing said monomer, and

c. chemically eroding away the original substrate material.

12. A method of manufacturing a highly regular, preferably triply-periodic, second microporous material characterized by the steps of: 50

a. infiltrating a polymer above its melting temperature into the pores of the first highly regular, preferably triply-periodic, microporous material made from a chemically erodible substrate material,

b. solidifying the polymer by lowering it below its melting temperature, and

c. chemically eroding away the first microporous substrate material.

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